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Topics in Quantum Mechanics

Chemistry

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Tranformation Theory

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Transformation Theory

References

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The general structure of quantum mechanical questions

There are three steps in every quantum mechanical experiment.

1 Prepare a system - make a measure on some observable

Let a state be prepared by measuring an observable $\hat{A}$. If

$$\hat{A}\,\psi_a = a\,\psi_a, \quad \{a, \psi_a\} \sim \text{the set of eigenvalues, eigenvectors of } \hat{A},$$

we can start the system in

$$\Psi(0) = \psi_a$$

by choosing systems for which an observation of $\hat{A}$ at $t = 0$ finds a.

2 Wait in time

If $\hat{H}\chi_n = E_n\chi_n$, the initial state

$$\Psi(0) = \sum_n \langle \chi_n | \psi_a \rangle\, \chi_n$$

evolves in time into

$$\Psi(t) = \sum_n e^{-iE_nt/\hbar} \langle \chi_n | \psi_a \rangle\, \chi_n.$$

3 Observe some quantity.

If $\hat{B}\,\phi_b = b\,\phi_b$, observation of $\hat{B}$ will reveal the value b with probability

$$|\langle \phi_b | \Psi(t) \rangle|^2 = \left| \sum_n \langle \phi_b | \chi_n \rangle\, e^{-iE_nt/\hbar} \langle \chi_n | \psi_a \rangle \right|^2. \tag{1}$$

probability of the value of B

Unitary transformations – a linear Transformation.

A transformation $\hat{U}$ is *linear* if

$$\hat{U}(a\,\psi_1 + b\,\psi_2) = a\,(\hat{U}\psi_1) + b\,(\hat{U}\psi_2)$$

for all a, b, ψ_1, ψ_2. A linear transformation $\hat{U}$ is *unitary* if

$$\left\langle \hat{U}\psi_1 | \hat{U}\psi_2 \right\rangle = \langle \psi_1 | \psi_2 \rangle$$

for all ψ_1, ψ_2.

The 3D vector analogue for this would be that

$$(\hat{U}\vec{v}) \cdot (\hat{U}\vec{w}) = \vec{v} \cdot \vec{w}$$

for all $\vec{v}, \vec{w}$. This is valid for *rotations* in 3D. Thus a unitary transformation is a complex, multidimensional extension of a rotation. [For *real* multidimensional vectors these are called *orthogonal* transformations.]

How do you know if a Transformation is unitary or NOT?

Matrix representations of unitary transformations

In an orthonormal basis set $\{\phi_n\}$, $\hat{U}$ would have a matrix representation

$$U_{mn} = \langle \phi_m | \hat{U}\phi_n \rangle.$$

If ψ_a, ψ_b are two (arbitrary) vectors with the matrix representations

$$\rightarrow\ \psi_a = \sum_n a_n\,\phi_n,$$

$$\rightarrow\ \psi_b = \sum_n b_n\,\phi_n,$$

then

$$\langle \psi_a | \psi_b \rangle = \sum_n a_n^* b_n.$$

Since

$$\hat{U}\psi_a = \sum_n a_n \hat{U}\phi_n = \sum_{n,k} a_n \langle \phi_k | \hat{U}\phi_n \rangle \phi_k = \sum_{k,n} \phi_k U_{kn} a_n,$$

$$\langle \hat{U}\psi_a | \hat{U}\psi_b \rangle = \sum_{k,m,n} U_{km}^* a_m^* U_{kn} b_n$$

Thus $\hat{U}$ is unitary $\Longleftrightarrow$

$$\sum_n a_n^* b_n = \sum_{k,m,n} U_{km}^* a_m^* U_{kn} b_n, \qquad \text{all } a_m, b_n$$

$$a_n^* = \sum_{k,m} a_m^* U_{km}^* U_{kn}, \qquad \text{all } a_m$$

$$\delta_{mn} = \sum_k U_{km}^* U_{kn}. \tag{2}$$

Now the inverse operator $\hat{U}^{-1}$ is the operator for which

$$\hat{U}^{-1} \cdot \hat{U} = \hat{1},$$

with $\hat{1}$ the *identity* operator. Since the matrix representation for $\hat{1}$ is δ_{mn},

$$\begin{aligned}\delta_{mn} &= \langle \phi_m | \hat{U}^{-1} \hat{U} | \phi_n \rangle \\ &= \sum_k \left[\hat{U}^{-1}\right]_{mk} U_{kn}.\end{aligned}$$

Comparison with (2) shows that $\hat{U}$ is *unitary* $\iff \left[\hat{U}^{-1}\right]_{mn} = U_{nm}^*$.

Contrast these two cases: If you transpose and take the complex conjugate of a matrix, you get

(i) the original matrix if the matrix represents an *Hermitian* operator,

(ii) the inverse of the original matrix if the matrix represents generates a *unitary* transformation.

Basis set transformations are unitary transformations

Let $\{\phi_n\}$ be an orthonormal basis set, let $\hat{T}$ be a linear transformation, and let

$$\psi_k = \hat{T} \phi_k$$

be the vector into which $\hat{T}$ transforms ϕ_k. In matrix form,

$$\psi_k = \sum_n \langle \phi_n | \hat{T} \phi_k \rangle \, \phi_n = \sum_n T_{nk} \, \phi_n$$

with

$$T_{nk} = \langle \phi_n | \psi_k \rangle = \langle \phi_n | \hat{T} \phi_k \rangle.$$

$\hat{T}$ will give a transformation to a new orthonormal basis set if

$$\begin{aligned}\delta_{k\ell} &= \langle\psi_k|\psi_\ell\rangle \\ &= \sum_{m,n}\langle T_{mk}\phi_m|T_{n\ell}\phi_n\rangle \\ &= \sum_{m,n} T^*_{mk}T_{n\ell}\langle\phi_m|\phi_n\rangle \\ &= \sum_n T^*_{nk}T_{n\ell}\end{aligned}$$

which shows (compare this with (2)) that T_{ij} is the matrix representation of a unitary transformation. That is, a 'rotation' of an orthonormal basis set gives a new orthonormal basis set.

The T_{nk} are, of course, the components of ψ_k in the basis set $\{\phi_n\}$. Writing $T_{nk} = \psi_k^{(n)}$,

$$T = \begin{bmatrix} \psi_1^{(1)} & \psi_2^{(1)} & \cdots \\ \psi_1^{(2)} & \psi_2^{(2)} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} = \left[\vec{\psi}_1 \,|\, \vec{\psi}_2 \,|\, \cdots\right]$$

The transpose of this matrix is

$$\tilde{T} = \begin{bmatrix} \psi_1^{(1)} & \psi_1^{(2)} & \cdots \\ \psi_2^{(1)} & \psi_2^{(2)} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} = \begin{bmatrix} \vec{\psi}_1 \\ \vec{\psi}_2 \\ \vdots \end{bmatrix}$$

If we take the complex conjugate of this array, it is clear that the product

$$T\cdot\tilde{T}^* = \left[\langle\psi_k|\psi_\ell\rangle^*\right] = [\delta^*_{k\ell}] = \hat{1}$$

and

$$\tilde{T}^*\cdot T = [\langle\psi_k|\psi_\ell\rangle] = [\delta_{k\ell}] = \hat{1}$$

Of course,

$$[T^{-1}]_{kn} = [T^*]_{nk} = \langle\psi_n|\phi_k\rangle^* = \langle\phi_k|\psi_n\rangle$$

are just the matrix elements of the reverse transformation, the transformation from the $\{\psi_k\}$ basis set to the $\{\phi_n\}$ basis set.

The quantum experiment revisited

Since $e^{-i\hat{H}t/\hbar}\chi_n = e^{-iE_nt/\hbar}\chi_n$, the probability of seeing 'b' after starting a system in ψ_a and waiting a time t can be written (that is, (1) can be rewritten)

$$\left|\sum_{m,n}\langle\phi_b|\chi_m\rangle\langle\chi_m|e^{-i\hat{H}t/\hbar}\chi_n\rangle\langle\chi_n|\psi_a\rangle\right|^2.$$

There are two basis set transformations. The unitary operator $\hat{R}$ with matrix elements $R_{na} = \langle\chi_n|\psi_a\rangle$ generates the basis set transformation $\{\psi_a\} \to \{\chi_n\}$.
The unitary operator $\hat{S}$ with matrix elements $S_{bn} = \langle\phi_b|\chi_n\rangle$ generates the basis set transformation $\{\chi_n\} \to \{\phi_b\}$.

Time evolution is associated with

$$U_{mn}(t) = \langle\chi_m|e^{-i\hat{H}t/\hbar}\chi_n\rangle = e^{-E_nt/\hbar}\delta_{mn}.$$

This is also a unitary transformation since

$$\sum_k U^*_{km}(t)U_{kn}(t) = \sum_k e^{iE_mt/\hbar}\delta_{km}e^{-iE_nt/\hbar}\delta_{kn} = \delta_{mn}.$$

Symbolically, time evolution is a linear transformation

$$\Psi(t) = \hat{U}(t)\Psi(0), \qquad \text{with} \quad \hat{U}(t) = e^{-i\hat{H}t/\hbar}$$

with $\hat{U}(t)$ a unitary transformation.

Putting all this together, the sought probability is

$$\left|\sum_{m,n} S_{bm}U_{mn}(t)R_{na}\right|^2 = \left|[\hat{S}\hat{U}(t)\hat{R}]_{ba}\right|^2.$$

The computational problem consists of making three unitary transformations. We start from a basis set fixed by $\hat{A}$, rotate to a basis set fixed by $\hat{H}$, rotate by $e^{-i\hat{H}t/\hbar}$, and then rotate to a basis set fixed by $\hat{B}$.

R
U Time evolution
S

The Emperor's New Mind

Roger Penrose